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THE DECOMPOSITION OF HYDROGEN SULPHIDE

A THESIS

BY

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This Thesis has been accepted by the Graduate School of New York University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

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I wish to record my indebtedness to Dr. H. Austin Taylor under whose direction this work was undertaken

THE DECOMPOSITION OF HYDROGEN SULPHIDE

BY CHARLES F. PICKETT[1]

The interest attached to the study of gaseous reactions and the elucidation of their mechanisms together with the present effort towards the discovery of purely unimolecular reactions suggested that the decomposition of hydrogen sulphide into hydrogen and sulphur might furnish such a reaction. The temperature at which such a reaction would proceed with measurable speed would necessitate the use of a quartz reaction system and even then the surface action might not be negligible. A preliminary investigation therefore was made of the reaction as it occurs on the surface of a hot filament, this being a convenient way of producing, locally, a high temperature.

The study of catalytic poisons points definitely to the inhibition which is brought about by sulphur compounds in general, and by hydrogen sulphide in particular. Maxted[2] has published a series of papers in which the inhibitory effects of several poisons, one of which is hydrogen sulphide, are discussed. It was shown that the adsorbing power of the platinum metals for hydrogen was greatly inhibited by hydrogen sulphide. When a small amount of tish gas was allowed to enter the reaction chamber, the amount of hydrogen adsorbed was very small. However, when the chamber was heated to 100°C and evacuated, a volume of hydrogen equal to that of the hydrogen sulphide first introduced, was obtained, but no hydrogen sulphide came off. If now the catalyst was again tested for its adsorptive power, it adsorbed some hydrogen though not as much as it did before being poisoned. The sulphur remaining obviously exerts also a poisoning effect.

Such facts immediately suggest that the adsorption of hydrogen sulphide by platinum is extremely high and that this metal therefore at a high temperature ought to be an efficient catalyst for its decomposition since the hydrogen formed will not be adsorbed in the presence of excess hydrogen sulphide: the sulphur alone possibly causing complications. The study of the reaction made has brought out this point quite clearly and furnishes too an interesting case of gaseous inhibition.

Experimental

The method adopted for the study consists, in outline, of passing hydrogen sulphide at known rates of flow over a platinum filament, heated electrically to a known temperature, the effluent gases being analysed to evaluate the extent of decomposition.

Hydrogen sulphide of 99.5 per cent purity can be readily prepared from calcium sulphide as recommended by Pollitzer[3]. Kahlbaum's chemically

[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

[2] J. Chem. Soc., **115**, 1050 (1919); **117**, 1280(1920); **119**, 225, (1921).

[3] Pollitzer: Z. anorg. Chem., **64**, 121 (1909).

pure calcium sulphide in lump form was used in an ordinary Kipp generator with a solution of hydrochloric acid, made by mixing equal parts of concentrated acid and distilled water. Before connecting the generator to the remainder of the apparatus about four liters of H_2S were drawn off to ensure the complete removal of air. The gas was first dried by passing over calcium chloride, and finally dried before entering the reaction chamber by passing over phosphorus pentoxide. The gas after passage through the reaction chamber was absorbed in an almost saturated solution of potassium hydroxide.

The rate of flow of the gas was controlled by a flow-meter necessitating a very steady pressure. For this purpose, two Kipp generators connected in parallel were connected to the generator and used as a gasometer. A three-way stopcock was used at the mouth of the gasometer so that it could be permanently connected with both the generator and the flow-meter. Since the gasometer contained water it also served to remove all traces of hydrogen chloride carried over from the generator.

The flow-meter was of the type described by Benton[1] for small rates of flow. The capillary was about one centimeter in length blown in Pyrex glass. Distilled water was used in the manometer and was of course saturated with hydrogen sulphide.

The reaction chamber was similar in construction to that used by Hinshelwood.[2] The chamber was blown of Pyrex glass about eleven centimeters long and three centimeters in diameter. A fine platinum wire about ten centimeters long was stretched axially across the tube, connections to the wire being made by mercury contacts through inner seals. The inlet and outlet for the gas was effected by sealing two pieces of glass tubing, one at each end and on opposite sides of the tube. The two tubes for the mercury contacts, as well as the inlet and outlet tubes were bent vertically, so that the reaction chamber could be immersed in melting ice, the ends of the tubes being above water. The end of the outlet tube was fitted with a ground-glass joint bent in a horizontal position to accommodate the absorption bulb. Before the outlet tube was completed a small wad of cotton wool was placed in the tube to prevent any sulpher from being carried over. It was found from preliminary experiments that solid sulphur in the form of a smoke was carried over with the effluent gases when the cotton wool was absent.

The absorption bulb was of special construction to meet the demands of the experiment. No absorption apparatus which allowed bubbling could be used since it would seriously affect the readings of the manometer levels in the flow-meter. The bulb used therefore consisted of a tube seven centimeters long and one and a half centimeters in diameter. At one end a small piece of tubing was sealed vertically then bent in a horizontal direction and furnished with a ground joint to fit the reaction chamber exit. To the other end, a bulb of four centimeters diameter was attached by a short length of small tubing and terminating at its upper end with a ground joint of one centimeter diameter, to allow the bulb to be filled with pieces of solid potassium hydroxide.

[1] J. Ind. Eng. Chem., **11**, 623 (1919).

[2] J. Chem. Soc., **127**, 327 (1925).

The stopper of this ground joint was drawn off to a small tube to accommodate a small rubber cover during weighing, thereby preventing the absorption of carbon dioxide. This form of absorption bulb allows the tube to be partially filled with a nearly concentrated solution of potassium hydroxide, the bulb carrying pieces of the solid. The effluent gases then pass over the liquid where most of the H_2S is absorbed, the moist solid finally removing the last traces.

The temperature of the filament was measured with a Hoskins optical pyrometer, a distinct image of the heated wire being obtained by using an

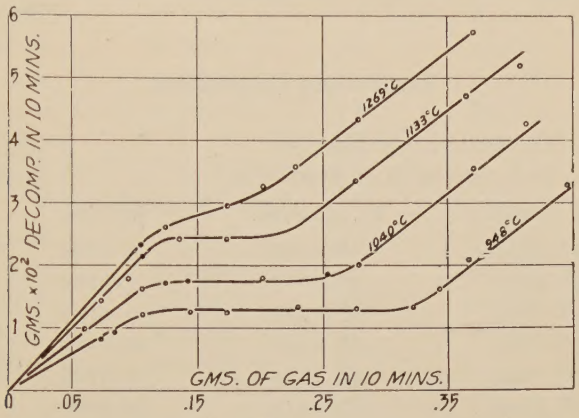

FIG. 1

auxiliary lens at the objective end of the telescope. The filament was maintained at constant temperature by manual operation of a rheostat in series with the platinum wire and two storage cells of six volts each. Any variation in the temperature would affect the resistance of the wire and hence alter the current, such variation registering itself on the ammeter connected in the circuit.

The flow-meter was calibrated by absorbing the hydrogen sulphide in potassium hydroxide for a definite time interval, the amount of gas absorbed being measured by the increase in weight of the absorption bulb. For the lower rates, up to 0.2g. the time interval was taken as ten minutes; above this rate of flow five minutes was deemed sufficient. A calibration curve for the flow-meter was made by plotting the difference of the levels of the manometer against the weight of gas per ten minutes.

The reaction chamber was cleaned and dried thoroughly, connected to the remainder of the apparatus by a short rubber connection and immersed in a bath of melting ice. Hydrogen sulphide was passed through until all the air had been swept out. The pressure was regulated to the desired rate of flow and maintained constant by manipulation of stopcocks. The platinum filament was then heated and the reaction allowed to proceed for a short time until equilibrium was established. The hydrogen sulphide which was undecomposed came over with the hydrogen, the sulphur being condensed on the walls of the reaction chamber. The hydrogen sulphide was absorbed by

the potassium hydroxide while the hydrogen passed through the absorption system. From the increase in weight of the absorption bulb, the amount of hydrogen sulphide decomposed could be obtained by difference from the known rate of flow. The average of six results was taken at each rate of flow.

Experiments were carried out at four different temperatures, namely: 948°C., 1041°C., 1138°C., and 1269°C. One example of a typical run is reproduced and a summary of the results at other rates of flow follows. The graph shows the four curves obtained at the different temperatures plotting the weight of gas decomposed against the rate of flow of gas, each per ten minutes.

Results and Calculations

Temperature of filament 1138°C.
H_2S passing in 10 mins. 0.0847g.

Run	Wt. of bulb	Wt. after abs.	Wt. abs.	Wt. decomp.
1	37.9632	38.0327	0.0695	0.0152
2	38.0327	38.1027	0.0700	0.0147
3	38.1027	38.1729	0.0703	0.0145
4	38.1729	38.2428	0.0697	0.0150
5	38.3140	38.3844	0.0704	0.0143
6	38.3844	38.4544	0.0700	0.0147
			Average	0.0147

Experiment 1.

Temperature of filament 948°C.

Run	Flow of Gas	Wt. decomp.	Run	Flow of Gas	Wt. decomp.
1	0.0740	0.0080	8	0.2310	0.0133
2	0.0847	0.0092	9	0.2772	0.0133
3	0.0955	0.0115	10	0.3219	0.0132
4	0.1058	0.0121	11	0.3430	0.0161
5	0.1268	0.0160	12	0.3661	0.0209
6	0.1448	0.0125	13	0.4086	0.0245
7	0.1732	0.0123	14	0.4462	0.0328

Experiment 2.

Temperature of filament 1041°C.

1	0.0591	0.0099	7	0.2018	0.0178
2	0.0835	0.0125	8	0.2278	0.0183
3	0.1058	0.0159	9	0.2534	0.0192
4	0.1250	0.0171	10	0.2782	0.0201
5	0.1418	0.0175	11	0.3262	0.0290
6	0.1736	0.0175	12	0.3714	0.0356
			13	0.4134	0.0427

Experiment 3.

Temperature of filament 1138°C.

Run	Flow of Gas	Wt. decomp.	Run	Flow of Gas	Wt. decomp
1	0.0740	0.0142	10	0.1058	0.0204
2	0.0847	0.0147	11	0.1448	0.0253
3	0.0955	0.0179	12	0.1732	0.0242
4	0.1063	0.0214	13	0.2310	0.0299
5	0.1170	0.0237	14	0.2772	0.0336
6	0.1268	0.0250	15	0.3219	0.0379
7	0.1357	0.0242	16	0.3661	0.0471
8	0.1447	0.0254	17	0.4086	0.0518
9	0.1530	0.0248	18	0.4462	0.0564

Experiment 4.

Temperature of filament 1269°C.

1	0.1058	0.0234	6	0.2278	0.0359
2	0.1250	0.0260	7	0.2782	0.0433
3	0.1418	0.0267	8	0.3262	0.0505
4	0.1736	0.0295	9	0.3714	0.0570
5	0.2018	0.0326			

The temperature coefficient, per ten degrees, calculated for the rates of the reaction which are independent of the rate of flow of the gas, that is, for the horizontal portions of the curves, gives between 948°C and 1041°C a value of 1.034 and between 1041°C and 1138°C a value of 1.035. Taking 1.035 as the average value in this region, namely 1315°K, the heat of activation calculated from the Arrhenius equation

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

where k is rate of reaction, E is the heat of activation per gram molecule, R is the gas constant per gram molecule, T is the absolute temperature, yields a value of 11,750 calories.

Discussion of Results

The results may be best discussed by referring to the curves shown previously. The general upward trend of the curves shows an increase in the decomposition with increasing flow of the gas at any given temperature. In the absence of any complicating factors, such a behavior would be expected, producing a curve rising slowly to a maximum, which would correspond to maximum frequency of collision between the hydrogen sulphide molecules and the platinum filament. At this point any further increase of flow would have little or no effect on the rate of decomposition, as expressed by the amount decomposed per unit of time.

The absence of such a smooth curve is conclusive proof that the decomposition is not so simple as visualised above, but must be complex, in such a way

that the complicating factor is opposed in its effect to the increased decomposition with increased flow of gas. That this is so is readily seen from the horizontal portions of the curves where temporarily the rate of decomposition is constant for a small range in the rate of flow. What this complicating factor is may be judged best from the fact that eventually an increase in the rate of flow can overcome it, so that the normal increased decomposition with increased passage of the hydrogen sulphide is once more established. Furthermore that the increase in rate of flow necessary to cause this is less at higher temperatures than at the lower ones so that eventually at sufficiently high temperatures the complicating factor has almost entirely disappeared, seems significant.

From our knowledge of the poisonous nature of sulphur to catalysts, particularly of the platinum group, it would seem probable that the sulphur resulting from the decomposition was the cause of the complications to which reference has been made. The work of Maxted (loc. cit.) has definitely established that complexes between platinum and sulphur are formed and exhibit remarkable stability. The adsorbed sulphur however, could not be the cause of the decreased decomposition since a mere increase in the rate of flow of gas is sufficient to correct this. This latter fact is extremely significant suggesting that the sulphur, immediately after adsorption, or during that process, probably forms a thin film of vapor around the filament thereby preventing the on-coming hydrogen sulphide from reaching the hot surface. Accepting this fact, the effect of increased temperature is at once apparent, since then the rate of vaporisation of sulphur from the hot platinum surface would be greater.

It would appear therefore, that the actual mechanism of the complete reaction consists primarily of adsorption of hydrogen sulphide molecules on the platinum surface, a decomposition resulting in the separation of hydrogen and a subsequent desorption or vaporisation of the residual sulphur from the platinum surface. Such a mechanism is in agreement with our present knowledge and at the same time will explain satisfactorily the results found here.

Adsorption of H_2S by a platinum catalyst occurs as Maxted has shown with definite orientation, the sulphur being immediate to the platinum surface. The subsequent decomposition of the hydrogen sulphide molecule would cause, therefore, hydrogen to be liberated first, leaving sulphur momentarily attached to the platinum. That such attachment could hold for long is not probable owing to the high temperature of the filament. The sulphur therefore would be volatilised immediately, during which process the thin sulphur atmosphere referred to above would be formed. At any particular temperature the life of such an atmosphere would depend partly on the rate of flow of hydrogen sulphide and partly on the rate of decomposition. These two factors are opposed to one another from the point of view of removal of the sulphur atmosphere, since the increased decomposition increases it, whilst the increased rate of flow decreases it. As the rate of flow is increased however, there is a tendency also to increase the rate of decomposition.

If the rate of increase of rate of flow is greater than the rate of increase of decomposition, the removal of the sulphur atmosphere will eventually be accomplished, requiring however, a definite increase at a particular temperature for that purpose. As the temperature of the filament is raised the increasing decomposition with decreasing rate of flow will be accompanied by an increasing rate of evaporation of the sulphur, so that although at any given rate of flow the actual amount of sulphur formed is greater at the higher temperature, the rate of its removal from the sphere of action will also be greater and require therefore a smaller increase in the rate of flow to complete the removal. Such a mechansim explains satisfactorily the decreasing horizontal portions of the curves with increasing temperature, and their eventual disappearance when the temperature is sufficiently high.

Accepting this then, as the mechanism of the reaction there remains only one portion of the curves which will furnish any quantitative information with regard to the reaction. That portion, is the horizontal portion, for here alone are the two opposing factors, balanced. On the remainder of the curves the effect of a rise of temperature will be a complex funtcion made up partly of the temperature effect on the pure chemical decomposition and partly of the temperature effect on the rate of evaporation of the sulphur.

On the horizontal portion of the curves the rate of decomposition is a constant independent of the rate of flow of the gas. The temperature coefficient must therefore be due solely to the change in rate of evaporation of the sulphur. The value of 11,750 calories previously obtained is therefore the heat of evaporation of sulphur. Norrish and Rideal[1] have shown that the energy necessary to break a S-S bond is approximately 12,500 calories. It seems reasonable to assume, that the affinity between sulphur and platinum will be less than this value, although from Maxted's work such complexes seem highly stable. The value 11,750 calories therefore would appear quite reasonable and would lend confirmation to the suggested mechanism of reaction.

Summary

1. The decomposition of hydrogen sulphide on a heated platinum filament has been studied by a dynamic method, at four temperatures in the neighborhood of 1000°C.

2. The curves illustrating the relation between decomposition and rate of flow of gas at these temperatures have been found. These show three branches, two of which show an increased amount of decomposition as the rate of flow is increased, separated by a third branch where the amount of decomposition is constant and independent of the rate of flow. The extent of this branch decreases as the temperature rises, so that at the highest temperature the curve shows merely a point of inflexion.

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[1] J. Chem. Soc., **123**, 3216 (1923).

3. The mechanism of the reaction suggested, consists of the primary adsorption of the hydrogen sulphide oriented with the sulphur atom to the platinum, a splitting of the adsorbed molecule, hydrogen being liberated and subsequent evaporation of sulphur from the heated filament.

4. The temperature coefficient for the horizontal branches was found to be 1.035 per ten degrees which is equivalent at these temperatures to a heat of evaporation of sulphur from the platinum surface of 11,750 calories.

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